



(19)

Europäisches Patentamt

European Patent Office

Offic e urop en d s br v ts



(11)

EP 0 822 207 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

04.02.1998 Bulletin 1998/06

(51) Int Cl. 6: C08G 18/40, C09J 175/04

(21) Application number: 97305696.3

(22) Date of filing: 29.07.1997

(84) Designated Contracting States:

AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE

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(30) Priority: 29.07.1996 US 681577

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### (54) Urethane laminating adhesives useful for retort pouches

(57) In a two-part, 100% solids adhesive composition useful for preparing a polymeric laminate adhesive pouch, a first part is a liquid OH-functional polyester con-

taining epoxy resin having both epoxy and hydroxyl functionality and a second part is a multi-functional isocyanate.

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**Description**

The present invention is directed to a urethane laminating adhesive for adhering polymeric films that may be formed into retort pouches for food or medicinal applications.

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**Background of the Invention**

Retort pouches for sterilizing food or medicinal substances are typically formed of two (or more) layers of polymeric film. Typically, an inner layer is formed of a material, such as cast polypropylene, which is heat-sealable and food- or medicine-compatible. A second layer, such as polyester or polyamide, is typically adhered to the inner layer for packaging strength. In addition, such a second layer as the outer layer may be printed with suitable inks.

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The present invention is directed to an adhesive composition suitable for use in adhering polymeric layers for food or medicinal retort pouches, which adhesive composition is free of or substantially free of organic solvents.

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**Summary of the Invention**

In accordance with the invention there is provided a two-part adhesive composition suitable for adhering polymeric layers to form laminates useful, for example, in forming retort pouches for food or medicinal applications. The two part adhesive composition comprises a first part I) having A) between about 50 and about 99 wt%, preferably between about 70 and about 90 wt%, based on total weight of A) plus B), of a hydroxyl-terminated polyester that is liquid at 20°C, the polyester having a hydroxyl functionality of between 2 and about 2.1 and a hydroxyl number of between about 50 and about 300, preferably between about 180 and about 250, B) between about 1 and about 50 wt%, preferably between about 10 and about 30 wt%, based on total weight of A) plus B) of an epoxy resin which is solid at 20°C and is dissolved within said polyester A), the epoxy resin B) having an epoxy equivalent weight of between about 500 and about 3000 and a hydroxyl number of between about 100 and about 250, and C) up to about 0.05 wt%, preferably at least about 0.005 wt% relative to total weight of A) plus B), of an isocyanate cure catalyst. A second part II) comprises a multi-functional isocyanate having an isocyanate functionality of between 2 and about 4, preferably at least about 2.3. The second part II) is provided relative to the total hydroxyl functionality of A) plus B) at an NCO/OH ratio of between about 0.9 and about 3.0, preferably between about 1.05 and about 1.5.

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**Detailed Description of Certain Preferred Embodiments**

Polyesters useful in accordance with the present invention are liquid at room temperature, i.e., 20°C. Preferably, the polyesters have low viscosities, i.e., 500 cps or below at 20°C, so that the polyester A) and absorbed epoxy resin B) form a liquid composition at 20°C that can be easily mixed with liquid polyisocyanate and applied as an adhesive layer to sheets of polymeric material. The polyester is linear or substantially linear, being formed primarily from dicarboxylic acids and diols. Diols are used in excess, whereby the polyester is OH-terminated. Aliphatic diols and dicarboxylic acids are preferred, although aromatic diols and dicarboxylic acids may also be used. In selection of diols and dicarboxylic acids for forming the polyester, consideration is given to compatibility with food and/or medicine. Suitable diols include, but are not limited to diethylene glycol, propylene glycol, ethylene glycol, hexane diol, butane diol, neopentyl glycol, etc. Suitable dicarboxylic acids include, but are not limited to adipic acid, terephthalic acid, isophthalic acid, sebatic acid, azelaic acid, etc. A slight amount of branching may be acceptable; thus, polyols, such as trimethylol propane, and polycarboxylic acids (and anhydrides), such as trimellitic anhydride, may be incorporated into the polyester chain. The hydroxyl functionality of the polyester provides the means by which the polyester is cross-linked with the polyisocyanate to form a cross-linked urethane. The polyester may have some acid functionality, i.e., up to an acid number of about 25, but no acid functionality is required or even desired. A currently preferred polymer is a copolymer of adipic acid and diethylene glycol having an OH number of about 210.

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An important aspect of the composition of the present invention is the inclusion of the solid epoxy resin B) in the composition of the present invention. Particularly suitable epoxy resins are bisphenol A epoxy resins having both epoxy and hydroxyl functionality as described above. The OH functionality of the epoxy resin provides that the epoxy resin is cross-linked in the urethane curing reaction. The purpose served by the epoxy functionality of the epoxy resin is uncertain. While Applicants are not bound by theory, it is believed that the epoxy resin serves to bind to and "repair" breaks in the polyester chains which occur when the adhesive is subject to retort conditions. In any event, it is found that polyester A) and polyisocyanate part II) alone do not form an adhesive which adequately withstands retort conditions. Suitable bisphenol-A epoxy resins sold commercially by Shell Chemical Company are EPON® 1007F and 1002F.

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Epoxy resins of this type are typically solid at 20°C; however, they dissolve into the polyester at the relative use levels herein to form a liquid composition (Part I)). A typical temperature for dissolving the epoxy resin in the polyester is 100°C.

While adhesion will be obtained without a catalyst C), reasonably fast cure time generally requires a catalyst, such as dibutyltin dilaurate.

5 The polyfunctional isocyanate has a functionality of at least 2 and preferably somewhat higher, i.e., at least about 2.3 to provide good cross-link density upon curing. The polyfunctional isocyanate may be a monomer or mixture of monomers such as 4,4'-diphenylmethane diisocyanate, 4,2'-diphenylmethane diisocyanate, toluene diisocyanate, hex-  
10 amethylene diisocyanate, isophoron diisocyanate, tetramethylxylene diisocyanate, etc, but preferably is polymeric, multi-functional isocyanate. A preferred multi-functional isocyanate is a trimer of hexane diisocyanate, the trimer having an isocyanate functionality of 3. Also suitable as multi-functional isocyanates are isocyanate-functional polymers, such as polyester urethanes and polyether urethanes. To facilitate mixing with part I), the multi-functional isocyanate must be liquid at 20°C.

10 Part II), the multi-functional isocyanate, is employed at least approximating and preferably in excess of the OH functionality of part I), including the polyester and the epoxy resin, i.e., at an NCO/OH ratio of between about 0.9 and about 3.0, preferably between about 1.05 and about 1.5, and most preferably between about 1.2 and about 1.4.

15 When parts I) and II) are mixed, curing begins immediately. Accordingly, the two parts are mixed at the point of application, typically within about 30 seconds of application of the mixture to one of the adhesive layers.

20 Laminates using the adhesive of the present invention are formed in a conventional manner. Typically, the two parts (I) and II)) are mixed and the mixture applied as a layer to one sheet of polymeric material. Shortly thereafter, the two sheets are nipped together with heat, e.g., 66-72°C, and pressure. An immediate bond is formed between the layers, although full cure takes place over a more extended period of time, e.g., a week. The fully cured adhesive will sustain a good bond between polymeric materials at typical retort conditions, e.g., 121°C at 15 p.s.i. for an hour.

25 Neither part (I) or II)) requires any organic solvent; thus, 100% solids adhesive compositions are provided in accordance with the present invention. While organic solvents may be added in minor amounts, e.g., up to about 2 wt% total, for viscosity adjustment or other purposes, from a volatile organic content (VOC) standpoint, addition of organic solvent is considered undesirable.

30 An important advantage of the adhesives of the present invention is that even at 100% solids, their viscosities are low, i.e., typically about 6,000 cps or below at 25°C and 950 cps or below at 50°C, 25 to 50°C being the preferred temperature application temperature of these adhesives. At these temperatures, it is possible to obtain coating weights as low as 1.14 g/m<sup>2</sup> coating weight on commercial machines running at 600 ft/min (183 meter/min.) speed, and coating weights between 1.14 and 1.47 g/m<sup>2</sup> coating weight are preferred for the adhesives of the present invention.

35 Low viscosity adhesives are advantage relative to higher viscosity adhesives which must be heated to higher temperatures in order to achieve commercially acceptable coating weights, typically around 1.63 g/m<sup>2</sup>. (When the coating weight is higher than 2.44 g/m<sup>2</sup>, the laminates tend to slide and adhesive tends to be squeezed out the sides.) Heating of urethanes to high temperatures can lead to evaporation of isocyanate and side reactions. Also, high viscosity adhesives tend to cause misting adhesive on the roll at high running speeds.

40 The invention will now be described in greater detail by way of specific examples.

#### Examples 1 and 2

45 Adhesive compositions were (example 1 in accordance with the invention, example 2 comparative) formulated as follows (in wt%):

Example	Polyester A*	Epoxy Resin**	HDI trimer
1	40	10	50
2	50		50

\*diethylene glycol adipate, OH no. 210

\*\*Epon® 1002F

50 Each example also contained 0.007 wt% dibutyltin dilaurate. Each adhesive composition was used to form a laminate of nylon and cast polypropylene, and the laminate used to form a retort pouch. Each pouch was filled with a 1:1:1 mixture of catchup/vinegar/corn oil, and the pouches were retorted at 121°C at 15 p.s.i. for an hour. Results are as follows:

Example	Appearance after retort	Bond strength after retort
1	no delaminating or tunneling	1,160 g/in
2	blistering	550 g/in.

## Claims

1. A 100 percent solids, two part adhesive composition consisting essentially of
  - 5 I) a first part comprising
    - A) from 50 to 99 wt%, based on total weight of (A) plus (B), of a hydroxyl terminated polyester; said polyester being liquid at 20°C and having a hydroxyl functionality of 2 to 2.1 and a hydroxyl number of 50 to 300,
    - 10 B) from 1 to 50 wt% of an epoxy resin based on total weight of (A) plus (B) which epoxy resin is solid at 20°C and is dissolved within said polyester (A), said epoxy resin (B) having an epoxy equivalent weight of 500 to 3000 and a hydroxyl number of 100 to 250, and
    - C) up to 0.05 wt% of an isocyanate cure catalyst relative to the weight of (A) plus (B), and
  - 15 II) a second part comprising a multi-functional isocyanate having an isocyanate functionality of 2 to 4, said second part (II) being provided relative to the total hydroxyl functionality of (A) plus (B) at an NCO/OH ration of 0.9 to 3.0.
2. An adhesive composition according to claim 1 wherein said hydroxyl terminated polyester (A) has an OH number from 180 to 250.
- 20 3. An adhesive composition according to claim 1 or claim 2 wherein said multi-functional isocyanate (II) has an isocyanate functionality of at least 2.3.
- 25 4. An adhesive composition according to any preceding claim wherein said catalyst (C) is provided in an amount at least 0.005 wt% relative to the weight of components (A) plus (B).
5. An adhesive composition according to any preceding claim wherein said multi-functional isocyanate is a trimer of hexane diisocyanate.
- 30 6. An adhesive composition according to any preceding claim wherein said polyester is a polymer of adipic acid and diethylene glycol.
- 35 7. An adhesive composition according to any preceding claim wherein said NCO/OH ratio is from 1.05 to 1.5.
8. An adhesive composition according to claim 7 wherein said NCO/OH ratio is from 1.2 to 1.4.
- 35 9. An adhesive composition according to any preceding claim wherein said first part I comprises from 70 to 90 wt% of said hydroxyl-terminated polyester (A) and from 10 to 30 wt% of said epoxy (B).
- 40 10. A laminate comprising a first polymeric layer and second polymeric layer adhered with an adhesive composition according to any preceding claim.
- 45 11. A laminate according to claim 10 wherein said first polymeric layer is polypropylene and said second polymeric layer is polyester.
12. A laminate according to claim 10 wherein said first polymeric layer is polypropylene and said second polymeric layer is polyamide.

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## EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)		
X	EP 0 349 838 A (TAKEDA CHEMICAL) * page 2, line 17 - page 5, line 31; claims 1-10 *	1,10	C08G18/40 C09J175/04		
A	EP 0 622 437 A (TAKEDA CHEMICAL) * page 2, line 45 - page 5, line 57; claims 1,7,10 *	1,10			
A	US 4 613 660 A (GOEL ET AL) * column 1, line 27 - column 3, line 50; claims 1-7; example 5 *	1			
A	EP 0 279 721 A (COMPAGNIE FRANCAISE DE PRODUITS INDUSTRIELS) * the whole document *	1			
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			TECHNICAL FIELDS SEARCHED (Int.Cl.6)		
			C08G C09J		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	4 November 1997	Bourgonje, A			
CATEGORY OF CITED DOCUMENTS					
X : particularly relevant if taken alone	T : theory or principle underlying the invention				
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